Pyrogenic silicon dioxide powder and dispersion thereof

The invention provides a pyrogenically produced silicon
dioxide powder, an aqueous dispersion containing this
silicon dioxide powder, the production and use of the
5   silicon dioxide powder and the dispersion.

The term pyrogenic silicon dioxide or pyrogenic silica
(fumed silica) is a collective term for all highly disperse
silicas obtained in the gas phase at elevated temperatures
by coagulation of monomeric silica. There are two processes
10   for the industrial production of pyrogenic silicas, high-
temperature hydrolysis and the arc process.

In the high-temperature hydrolysis process a homogeneous
mixture of a vaporous silicon compound, hydrogen, oxygen
and an inert gas is burned with a burner in a cooled
15   combustion space. Two reactions proceed side by side here.
Firstly the reaction of hydrogen and oxygen with formation
of water and secondly the hydrolysis of the silicon
compound with formation of silicon dioxide.

The homogeneity of the gas mixture means that the reaction
20   conditions and hence the formation and growth conditions
are largely the same for each SiO_2 particle, such that very
homogeneous and uniform particles can form. Air is used as
the oxygen source in the known process. The pyrogenic
silicas produced by the known process display specific
25   surface areas of between 10 and 600 m^2/g.

The starting material for the silicon dioxide is generally
silicon tetrachloride (cf. Ullmann's Encyclopedia of
Industrial Chemistry, Vol. A23, pages 635 ff. 5th edition).
In addition to silicon tetrachloride methyl
30   trichlorosilane, trichlorosilane or mixtures thereof with
silicon tetrachloride can also be used.

JP 2002114510 claims a process in which silicon dioxide is obtained with an average particle size of 0.05 to 5 μm. In this process silicon compounds are burned in the presence of oxygen and hydrogen. Siloxanes, silanes or silicon

5 chlorides can be used as the silicon compound. However, the silicon dioxide produced by this process displays no properties that could not also be obtained by processes of the prior art. The process described is itself only of limited suitability for the production of larger

10 quantities. A non-uniform product and, where carbon-containing silicon compounds are used as starting materials, dark products too are then to be expected in particular.

When used in dispersions such as are used in the production

15 of glass articles or in chemical mechanical polishing in the semiconductor industry, the powder produced according to JP 2002114510 provides no advantages over the prior art.

Due to growing requirements an improvement in the properties of silicon dioxide is demanded in these very

20 sectors. In the glass industry in particular, highly filled, readily manageable dispersions, in other words ones with low viscosity, are required because of their low shrinkage on drying and sintering.

The object of the invention is to provide a silicon dioxide

25 powder which is suitable for the production of highly filled dispersions with low viscosity. The object of the invention is also to provide a stable dispersion containing this silicon dioxide powder.

The invention provides a pyrogenically produced silicon

30 dioxide powder having a specific surface area of between 5 and 600 m^2/g and a carbon content of less than 500 ppm, which is characterised in that it displays

- a specific dibutyl phthalate absorption of less than
  or equal to 1.2 g dibutyl phthalate/100 g SiO_2 per
  m^2 of specific surface area

- and a specific thickening action of less than
  15 mPas per m^2 of specific surface area.

The specific dibutyl phthalate absorption represents a
measure of the structure of the silicon dioxide powder
according to the invention as a function of its specific
surface area. The term structure in this connection means
the degree of intergrowth of the primary particles. These
are initially formed in the pyrogenic process and as the
reaction continues can coalesce to form chain-like
aggregates, which in turn form agglomerates. The specific
dibutyl phthalate absorption of less than or equal to 1.2 g
dibutyl phthalate/100 g SiO_2 per m^2 of specific surface
area claimed for the silicon dioxide powder according to
the invention is generally lower than pyrogenic silicon
dioxide powders obtained by the prior art.

The silicon dioxide powder according to the invention
arises only in combination with a specific thickening
action. This is understood to mean the thickening action
per m^2 of specific surface area. The thickening action is
determined in a dispersion of a silicon dioxide powder in a
polyester.

In a preferred embodiment the powders according to the
invention can display a specific compacted bulk density,
defined as the product of the compacted bulk density and
specific surface area, of between 1000 and 10000 and
particularly preferably between 4000 and 7000 g/l x m^2 of
specific surface area. Powders according to the invention
displaying a specific compacted bulk density in this range
can be incorporated especially readily into dispersions.

Furthermore, silicon dioxide powders according to the invention can preferably have a chloride content of less than 50 ppm, particularly preferably less than 20 ppm. The low chloride contents can for example demonstrate advantageous effects when the powders according to the invention are used in the area of chemical mechanical polishing.

The invention also provides a process for the production of silicon dioxide powder according to the invention which is characterised in that

- vaporous tetramethoxysilane (TMOS) and/or tetraethoxysilane (TEOS) together with air or with oxygen-enriched air and separately

- hydrogen

- are supplied to a burner, and the mixture of gases is allowed to react in a flame in a reaction chamber connected in series to the burner, and the solid reaction product is separated from the gas stream by known means,

- the lambda value in the burner being between 0.95 and 1.5 and

- sufficient secondary air also being supplied to the reaction chamber that the lambda value in the reaction chamber is between 0.8 and 1.6.

Figure 1 shows a simplified process flow chart upon which the process according to the invention is based. A = burner; B = flame; C = reaction chamber; 1 = supply of mixture comprising vaporous tetramethoxysilane and/or tetraethoxysilane together with air or with oxygen-enriched air; 2 = supply of hydrogen; 3 = supply of secondary air.

In the performance of the process it is substantial that a premixing of silane and air occurs, the stoichiometry of air/hydrogen and the oxygen component, expressed as the lambda value, being maintained in the burner and reaction
5   chamber.

Lambda denotes the ratio of oxygen supplied to the burner or the reaction chamber to stoichiometrically required oxygen, which is needed to convert the silane compound completely to silicon dioxide. The lambda value range that
10   must be maintained in the reaction chamber likewise refers to the total amount of the silane to be hydrolysed.

In the process according to the invention the volume ratio of oxygen/hydrogen in the burner can be varied between 0.2 and 2.8. In a particularly preferred embodiment the volume
15   ratio of oxygen/hydrogen in the burner is between 0.9 and 1.4.

Depending on the desired specific surface area, it can be useful to vary the streams supplied to the burner and the burner geometry in such a way that the discharge velocity
20   of the gases leaving the burner is at least 10 ms^{-1}. Discharge velocities of at least 20 ms^{-1} are particularly preferred.

The invention also provides an aqueous dispersion containing the silicon dioxide powder according to the
25   invention.

The aqueous dispersion according to the invention can display a content of silicon dioxide powder of between 20 and 80 wt.%. Dispersions having a content of silicon dioxide powder of between 40 and 60 can be particularly
30   preferred. These dispersions display a particularly high stability with a comparatively low structure.

The aqueous dispersion according to the invention can preferably display an average particle size in the

aggregates of silicon dioxide powder which is less than 200 nm. For certain applications such as e.g. the chemical mechanical polishing of semiconductor substrates, a value of less than 150 nm can be particularly preferred.

5   The dispersion according to the invention can be stabilised by the addition of bases or cationic polymers or aluminium salts or a mixture of cationic polymers and aluminium salts or acids.

Bases that can be used are ammonia, ammonium hydroxide,
10   tetramethyl ammonium hydroxide, primary, secondary or tertiary organic amines, sodium hydroxide solution or potassium hydroxide solution.

Cationic polymers that can be used are examples having at least one quaternary ammonium group, phosphonium group, an
15   acid adduct of a primary, secondary or tertiary amine group, polyethylene imines, polydiallylamines or polyallylamines, polyvinylamines, dicyandiamide condensates, dicyandiamide-polyamine cocondensates or polyamide-formaldehyde condensates.

20   Aluminium salts that can be used are aluminium chloride, aluminium hydroxychlorides having the general formula $Al(OH)_xCl$ where x=2-8, aluminium chlorate, aluminium sulfate, aluminium nitrate, aluminium hydroxynitrates having the general formula $Al(OH)_xNO_3$ where x=2-8,
25   aluminium acetate, alums such as aluminium potassium sulfate or aluminium ammonium sulfate, aluminium formate, aluminium lactate, aluminium oxide, aluminium hydroxide acetate, aluminium isopropylate, aluminium hydroxide, aluminium silicates and mixtures of the aforementioned
30   compounds.

Inorganic acids, organic acids or mixtures of the aforementioned can be used as acids.

In particular, phosphoric acid, phosphorous acid, nitric acid, sulfuric acid, mixtures thereof and their acid-reacting salts can be used as inorganic acids.

Organic acids that are preferably used are carboxylic acids having the general formula $C_nH_{2n+1}CO_2H$, where n=0-6 or n= 8, 10, 12, 14, 16, or dicarboxylic acids having the general formula $HO_2C(CH_2)_nCO_2H$, where n=0-4, or hydroxycarboxylic acids having the general formula $R_1R_2C(OH)CO_2H$, where R_1=H, R_2=CH_3, CH_2CO_2H, $CH(OH)CO_2H$, or phthalic acid or salicylic acid, or acid-reacting salts of the aforementioned acids or mixtures of the aforementioned acids and salts thereof.

Stabilisation of the dispersion according to the invention with tetramethyl ammonium hydroxide or aluminium hydroxychloride in an acid medium can be particularly advantageous.

The dispersion can optionally also contain other additives. These can for example be oxidising agents such as hydrogen peroxide or per-acids, oxidation activators whose purpose is to increase the rate of oxidation, corrosion inhibitors such as e.g. benzotriazole. Surface-active substances of a non-ionic, cationic, anionic or amphoteric nature can also be added to the dispersion according to the invention.

The invention also provides a process for the production of the dispersion according to the invention, which is characterised in that the silicon dioxide powder according to the invention is incorporated with a dispersing device into water, which can be stabilised by the addition of bases or cationic polymers or aluminium salts or a mixture of cationic polymers and aluminium salts or acids, and is then dispersed further for a period of 5 to 30 minutes.

There is no restriction on the type of dispersing device. It can be advantageous however, especially for the production of highly filled dispersions, to use dispersing

devices with a high energy input. These can for example be
rotor-stator systems, planetary compounders or high-energy
mills. In the latter, two predispersed streams of
suspension under high pressure are decompressed through a

5 nozzle. The two jets of dispersion hit each other exactly
and the particles grind themselves. In another embodiment
the predispersion is likewise placed under high pressure,
but the particles collide against armoured sections of
wall. A rotor-stator system can preferably be used to

10 produce the dispersion according to the invention.

The invention also provides the use of the silicon dioxide
powder according to the invention as a filler in rubber,
silicone rubber and plastics, to adjust the rheology in
paints and coatings and as a support for catalysts.

15 The invention also provides the use of the dispersion
according to the invention for the production of glass
articles, for chemical mechanical polishing and for the
production of inkjet papers.

Examples

Analytical determinations

The specific surface area of the powders is determined in accordance with DIN 66131.

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The dibutyl phthalate absorption is measured with a RHEOCORD 90 device supplied by Haake, Karlsruhe. To this end 8 g of the silicon dioxide powder is introduced into a mixing chamber with an accuracy of 0.001 g, the chamber is
10 closed with a lid and dibutyl phthalate is metered in through a hole in the lid at a predefined feed rate of 0.0667 ml/s. The compounder is operated at a motor speed of 125 revolutions per minute. On reaching the maximum torque the compounder and DBP metering are automatically switched
15 off. The DBP absorption is calculated from the consumed amount of DBP and the weighed amount of particles according to the formula below:

DBP value (g/100 g) = (DBP consumption in g / weighed amount of particles in g) x 100.

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The thickening action is determined by the following method: 7.5 g silicon dioxide powder are introduced into 142.5 g of a solution of an unsaturated polyester resin in styrene with a viscosity of 1300 +/- 100 mPas at a
25 temperature of 22°C and dispersed by means of a high-speed mixer at 3000 min^{-1}. A suitable example of an unsaturated polyester resin is Ludopal® P6, BASF. A further 90 g of the unsaturated polyester resin in styrene are added to 60 g of this dispersion and the dispersion process is repeated. The
30 thickening action is taken to be the viscosity value in mPas of the dispersion at 25°C, measured with a rotary viscometer at a shear rate of 2.7 s^{-1}.

The chloride content of the silicon dioxide powder is determined by the following procedure: Approximately 0.3 g of the particles according to the invention are weighed in accurately, topped up with 20 ml of 20 percent reagent-grade sodium hydroxide solution, dissolved and transferred into 15 ml cooled HNO_3 whilst being stirred. The chloride content in the solution is titrated with $AgNO_3$ solution (0.1 mol/l or 0.01 mol/l).

The carbon content of the silicon dioxide powder is determined by the following procedure: Approximately 100 to 1000 mg of the particles according to the invention are weighed accurately into a crucible, combined with 1 g each of ultrapure iron and aggregate (LECOCELL II) and burned in a carbon analyser (LECO) at approx. 1800°C with the aid of oxygen. The CO_2 that is generated is measured by IR and the content calculated therefrom.

The compacted bulk density is determined by reference to DIN ISO 787/XI K 5101/18 (not screened).

The pH is determined by reference to DIN ISO 787/IX, ASTM D 1280, JIS K 5101/24.

The viscosity of the dispersions is determined with a Physica Model 300 rotary rheometer and a CC 27 measuring beaker at 25°C. The viscosity value is determined at a shear rate of 10 1/sec. This shear rate is in a range in which the viscosity of the dispersions formed is virtually independent of the shear stress.

The particle size prevailing in the dispersion is determined by means of dynamic light scattering. A Zetasizer 3000 HSa (Malvern Instruments, UK) is used. The volume-weighted median value of the peak analysis is stated.

Example 1:

1.5 kg/h tetramethoxysilane are evaporated at 180°C and
introduced into the central pipe of the burner. 12 m³/h of
air are additionally introduced into the central pipe.
5   1.8 m³/h of hydrogen are fed into a pipe surrounding the
central pipe. The gas mixture burns in the reaction
chamber, into which 17 m³/h of secondary air are
additionally introduced.

The reaction gases and the silicon dioxide that is formed
10 are drawn through a cooling system by application of a
partial vacuum, cooling them to values between 100 and
160°C. The solid is separated from the waste gas stream in
a filter or cyclone.

The analytical data for the silicon dioxide powder obtained
15 is reproduced in Table 2.

Examples 2 to 9 and comparative examples 10 and 11 were
performed in the same way.

In comparative examples 12 to 14 silicon tetrachloride is
used in place of tetramethoxysilane. In these experiments,
20 following separation from the waste gas stream the silicon
dioxide powder is treated at elevated temperature with
water vapour-containing air to remove adhering hydrochloric
acid residues.

The physical-chemical data for the silicon dioxide powders
25 obtained is reproduced in Table 2.

Examples 1 to 9 lead to the silicon dioxide powders
according to the invention having a low structure,
expressed as the specific DBP value, a low specific
thickening action and a high specific compacted bulk
30 density.

Examples 10 and 11 show that only the process according to
the invention leads to these powders. Reducing the
secondary air or even omitting it altogether or increasing
the burner air does not lead to the silicon dioxide powders
5   according to the invention.

In the same way, using silicon tetrachloride, examples 12
to 14, whilst maintaining the conditions with regard to the
lambda value in the burner and in the reaction chamber,
does not lead to the silicon dioxide powders according to
10   the invention.

Example 15: Production of a dispersion in the acid pH range

36 kg of demineralised water are placed in a 60 l stainless
steel batch container. 6.4 kg of the pyrogenically
15   produced silicon dioxide are then drawn in under shear
conditions using the suction pipe of the Ystral Conti-TDS 3
and on completion of the drawing-in process shearing is
continued for a further 15 min at 3000 rpm.

20   Example 16: Production of a dispersion in the alkaline pH
range

35.5 kg of demineralised water and 52 g of a 30% KOH
solution are placed in a 60 l stainless steel batch
container. 6.4 kg of the pyrogenically produced silicon
25   dioxide are then drawn in under shear conditions using the
suction pipe of the Ystral Conti-TDS 3 and on completion of
the drawing-in process shearing is continued for a further
15 min at 3000 rpm. During this 15-minute dispersion the pH
is adjusted to and held at a pH of 10.4 by addition of
30   further KOH solution. A further 43 g of KOH solution were
used in this process and a solids concentration of 15 wt.%
established by addition of 0.4 kg water.

Example 17: Production of a dispersion in the presence of aluminium salts

35 kg of demineralised water are placed in a 60 l stainless
steel batch container. 6.4 kg of the pyrogenically
produced silicon dioxide are then drawn in under shear
conditions using the suction pipe of the Ystral Conti-TDS
3. 640 g of a 1 wt.% solution (relative to aluminium oxide)
of aluminium chloride are then added with dispersion and on
completion of the addition shearing is continued for a
further 15 min at 3000 rpm. 0.1 kg demineralised water and
305 g 1 N NaOH are then added to obtain a 15 wt.%
dispersion with a pH of 3.5.

Example 18: Production of a dispersion of Aerosil 90 (comparative example)

35.5 kg of demineralised water and 52 g of a 30% KOH
solution are placed in a 60 l stainless steel batch
container. 5.2 kg of AEROSIL® 90 are then drawn in under
shear conditions using the suction pipe of the Ystral
Conti-TDS 3 and on completion of the drawing-in process
shearing is continued for a further 15 min at 3000 rpm.
During this 15-minute dispersion the pH is adjusted to and
held at a pH of 10.4 by addition of further KOH solution. A
further 63 g of KOH solution were used in this process and
a solids concentration of 15 wt.% established by addition
of 0.6 kg water.

The physical-chemical parameters for the dispersions are
reproduced in Table 3.

Table 3: Physical-chemical data for the dispersions

	SiO$_2$	Concentration	pH	Average particle size	Viscosity (10s^{-1})
Ex.		[wt.%]		[nm]	[mPas]
15	From ex. 7	15	3.7	101	4.1
16	From ex. 7	15	10.4	103	1.9
17	From ex. 7	15	3.5	107	2.4
18	Aerosil 90*	12.5	10.4	198	3.5

*Pyrogenically produced silicon dioxide from Degussa AG, BET surface area approx. 90 m^2/g.

5   Example 19: Dispersion with high solids content

35.5 kg of demineralised water in a 60 l stainless steel batch container are adjusted to a pH of 11 with tetramethyl ammonium hydroxide solution (25%). 37 kg of the pyrogenically produced silicon dioxide are then drawn in
10 under shear conditions using the suction pipe of the Ystral Conti-TDS 3 and on completion of the drawing-in process shearing is continued for a further 15 min at 3000 rpm. During this 15-minute dispersion the pH is held at a pH of between 10 and 11 by addition of tetramethyl ammonium
15 hydroxide solution. A solids concentration of 50 wt.% is established by addition of the remaining amount of water that is needed.

The resulting dispersion has a silicon dioxide content of 50 wt.% and a pH of 10.3. It displays a viscosity,
20 determined with a Physica viscometer, of 2450 mPas. The average particle size is 116 nm. The dispersion displays no thickening or sedimentation even after a storage period of 6 months.

The silicon dioxide powders according to the invention are
25 characterised by an ability to be incorporated rapidly into aqueous media.

In comparison to dispersions with the known silicon dioxide
powder, the dispersions according to the invention display
more favourable values for viscosity and smaller particle
sizes.

5   Example 19 shows that dispersions with a high solids
content can also be produced. Under similar conditions the
use of known silicon dioxide powders with a comparable BET
surface area leads to gel-like compositions, or the powder
cannot be incorporated fully.

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Table 1: Amounts used and settings from examples 1 to 14

Example	TMOS [kg/h]	H$_2$ burner [m³/h]	Air burner [m³/h]	Secondary air [m³/h]	Lambda burner	Lambda reaction chamber	O$_2$/H$_2$ burner	v* [m/s]
1	1.5	1.8	12	17	1.11	2.32	1.4	30.0
2	1.5	2.3	12	17	1.01	2.09	1.1	31.0
3	1.5	3.4	14.8	17	1.02	1.96	0.9	39.1
4	1.5	2.4	14.8	17	1.19	2.27	1.3	37.0
5	1.5	3	14.8	17	1.08	2.07	1.0	38.2
6	1.5	2.4	12	17	1.00	1.88	1.1	31.2
7	1.5	2.4	12	17	1.00	1.83	1.1	31.2
8	1.5	2.4	12	17	1.00	2.09	1.1	31.2
9	1.5	1.8	12	17	1.11	2.31	1.4	30.0
Comp. ex.								
10	1.5	1.8	12	0	1.11	1.05	1.4	30.0
11	1.5	1.8	12	5	1.11	1.05	1.4	30.0
12**	4.4	2	5.8	17	1.21	3.79	0.61	17.6
13	4.4	2	5.2	17	1.09	3.68	0.55	16.3
14	4.4	2.3	5.5	17	1	3.30	0.50	17.6

* = Discharge velocity from burner; **12 to 14: SiCl$_4$ in place of TMOS

Table 2: Physical-chemical values of the silicon dioxide powders from examples 1 to 14

Example	BET [m²/g]	DBP number [g/100g]	Spec. DBP number [g/100g/[m²/g]	Thick-ening [mPas]	Spec. thick-ening [mPas]/[m²/g]	Comp. bulk density [g/l]	Spec. comp. bulk density [g/l]x[m²/g]	pH	c µg/g	Cl µg/g
1	200	225	1.1	1920	9.6	24	4800	4.24	< 100	< 13
2	129	146	1.1	770	5.9	35	4515	4.36	< 100	< 10
3	163	98	0.6	830	5.1	30	4890	4.38	< 100	< 10
4	330	314	1.0	2220	6.7	19	6270	3.98	< 100	< 10
5	196	125	0.6	1650	8.4	26	5096	4.05	< 100	< 13
6	109	74	0.7	690	6.3	42	4578	4.53	< 100	< 10
7	99	110	1.1	1325	13.4	50	4950	4.22	< 100	< 10
8	130	95	0.7	740	5.7	35	4550	4.13	< 100	< 10
9	191	191	1.0	1590	8.3	21	4011	4.00	< 100	< 14
Comp. ex.										
10	205	320	1.6	3100	15.1	n.d.*	n.d.	4.11	<100	<13
11	198	280	1.4	3050	15.4	n.d.	n.d.	4.09	<100	<10
12	199	346	1.7	3230	16.2	17	3383	4.09	< 100	80
13	131	309	2.4	1880	14.4	19	2489	4.17	< 100	44
14	91	233	2.6	2805	30.8	24	2184	4.23	< 100	83

* n.d. = not determined